<International Research Center for Elements Science> Organic Main Group Chemistry

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SUN, Yedi (UG) University of Toronto, Canada, 10 May - 20 August 2004

Scope of Research

Our research is concerned with some new aspects in the elemento-organic chemistry, including (1) elucidation of the σ-conjugation in the polysilane framework using the configuration-constrained oligosilane model systems, (2) development of intramolecular electron transfer systems through σ-conjugated oligosilane chains, (3) construction and application of new polycyclic systems including main group elements, (4) development of new efficient reactions using main group element reagents and transition metal complex catalysts, and (5) design and synthesis of novel π-conjugated systems containing main group elements.

Research Activities (Year 2004)

Presentations

My Favorite Silicon and Boron (invited), Tamao K, Herbert C. Brown Lecture, 3 April, Purdue University, USA.

Sigma-Conjugated Oligosilanes – Conformation Dependence of the Photophysical Properties (invited), Tamao K, Tsuji H, 17th IUPAC Conference on Physical Organic Chemistry (ICPOC17), 15 - 20 August, Shanghai, China.

Palladium-Catalyzed Cross-Coupling Reaction of Aryltriazene with Organometallic Reagents, Saeki T, Son E-C, Matsunaga T, Tamao K, 51st Symposium on Organometallic Chemistry, 22 October, Tokyo, Japan.

Elemento-Organic Chemistry Directed toward Materials Science, Tamao K, The First International Symposium on Functional Innovation of Molecular Informatics (invited), 13 - 15 October, Kyushu University, Fukuoka, Japan.

Elemento-Organic Chemistry Directed toward Materials Science, Tamao K, The 2nd International Symposium of the 21COE Program, Center for Practical Nano-Chemistry, 21 - 22 December, Waseda University, Tokyo, Japan.

Grants

Tamao K, Elements Science towards Construction of Organic and Inorganic Frameworks Focusing on Quality of Elements, Grant-in-Aid for Scientific Research on COE, April 2000 - March 2005.

Tsuji H, Development of New Method of Controlling Silicon Chain Conformation Aiming at Controlling Photophysical Properties of Oligosilanes, Grant-in-Aid for Young Scientists (B), April 2003 - March 2005.

Tsuji H, Synthesis and Photophysical Properties of Porphyrin-Oligosilane Hybrid Molecules, Grant-in-Aid on Priority Areas, April 2004 - March 2006.

Awards

Tamao K, Medal with Purple Ribbon, 29 April.

Tsuji H, Inoue Research Award for Young Scientists, Syntheses and Photophysical Properties of Oligosilane Conformationally Constrained by Methylene Tethers, Inoue Foundation for Science, 4 February.

Tsuji H, Progress Award in Silicon Chemistry, Japan,

The *All-Anti* Pentasilane

Recent studies have been unveiling the conformation dependence of the oligosilane σ conjugation: the *anti* conformation (SiSiSiSi dihedral angle ω = 180°) effectively extends the conjugation. For the highly conjugated system, it is desirable to control the silicon backbone precisely to *anti.* However, the peralkylated poly- and oligosilanes possess many kinds of conformers with smaller dihedral angles as energy minima, while the *anti* conformation corresponds to a local maximum on the energy surface. To overcome this problem, we have designed a bis(tetramethylene)-tethered bicyclic trisilane and prepared a pentasilane **1** with *all-anti* conformation.

The X-ray crystallography was performed on the diphenyl-substituted pentasilane as shown in Figure 1. The dihedral angles in the silicon backbone are 179.00(5)° and 179.11(5)°. The conformation of this compound is the closest to the ideal *all-anti* among the synthesized oligosilanes so far. UV absorption band of **1** corresponding to the lowest-energy σσ* transition is much narrower even at room temperature as compared with *n*-Si_5Me_{12}. The MCD of the pentasilane **1** show the characteristic signal to *all-anti* conformation as well. These results demonstrate the effectiveness of the bicyclic trisilane unit for the conformation control in the silicon backbone.

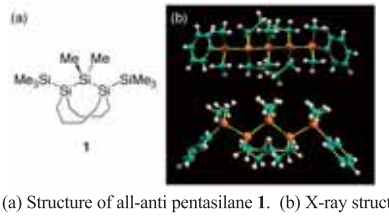


Figure 1. (a) Structure of all-anti pentasilane **1**. (b) X-ray structure of the *all-anti* pentasilane derivative.

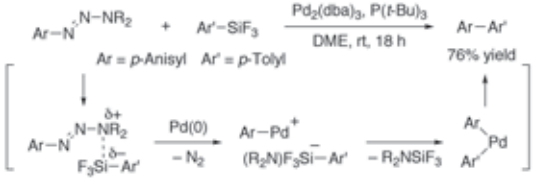
Reference: Tsuji H, Fukazawa A, Yamaguchi S, Toshimitsu A, Tamao K *Organometallics* **2004**, 23, 3375-3377.

Cross-Coupling Reaction of 1-Aryltriazenes with Organotrifluorosilanes

We have recently reported that the cross-coupling reaction of 1-aryltriazenes with areneboronic acids readily proceeds in the presence of a palladium catalyst, a phosphine ligand, and a Lewis acid such as boron trifluoride (Scheme 1). The Lewis acid–base interaction between the boron trifluoride and the terminal nitrogen atom of the triazene might be essential to enhance the oxidative addition of the carbon–nitrogen bond to the zero-valent palladium complex.

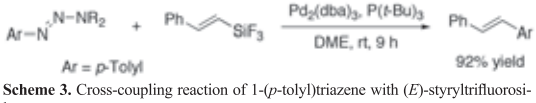
Scheme 1. Cross-coupling reaction of 1-aryltriazenes with areneboronic acids.

We have found a similar cross-coupling reaction with organosilicon compounds, instead of the boronic acids. Among the organosilicon compounds examined, only the most Lewis acidic trifluorosilane afforded the desired biaryl product. In this reaction, the addition of the external Lewis acid turned out not to be necessary, and finally the biaryl product was obtained in 76% yield (Scheme 2).



Scheme 2. Cross-coupling reaction of 1-aryltriazene with aryltrifluorosilane (plausible reaction mechanism).

The reaction system is applicable to the cross-coupling reaction with alkenyl-trifluorosilanes. As a typical example, the reaction of 1-(*p*-tolyl)triazene with (*E*)-styryltrifluorosilane readily proceeded at room temperature to afford the corresponding stilbene in 92% yield (Scheme 3).



Scheme 3. Cross-coupling reaction of 1-(*p*-tolyl)triazene with (*E*)-styryltrifluorosilane.

It is notable that the addition of methanol accelerates the coupling reaction in some cases. This effect is most remarkable for sterically hindered alkenyl silanes.

[1] T. Saeki, E.-C. Son, K. Tamao, *Org. Lett,* **2004**, 6, 617., [2] T. Saeki, T. Matsunaga, E.-C. Son, K. Tamao, *Adv. Synth. Catal.* **2004**, 346, 1689.

Control of Conformation and Photophysical Properties of Oligosilanes Based on Bicyclic Structure, The Society of Silicon Chemistry, Japan, 29 October.

Tsuji H, The ICR Award for Young Scientists, Conformation Control of Oligosilanes Based on Bicyclic Structure, ICR, 3 December.

Fukazawa A, Best Poster Award for Graduate Students, ICR, Conformation Control of Oligosilanes Based on Bicyclic Trisilane Unit, ICR, 5 March.

Fukazawa A, Symposium Poster Award, 51th Symposium on Organometallic Chemistry, Japan, 15 December.